WIDOM ALGORITHM FOR THE CHEMICAL POTENTIAL

We work in the canonical ensemble

$$Q(N,V,T) = \frac{1}{N!\lambda^{3N}} \int d^{3N}q \; e^{-\beta U(q_1 \cdots q_N)}$$

$$F(N,V,T) = -kT \ln Q(N,V,T)$$

$$= F^{(id)} + F^{(exc)} \qquad F^{(exc)} = -kT \ln\left(\frac{Z}{V^N}\right)$$

with $Z = \int d^{3N}q \; e^{-\beta U(q_1 \cdots q_N)}$

By definition $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$, $\mu^{(id)} = \left(\frac{\partial F^{(id)}}{\partial N}\right)_{V,T}$, $\mu^{(exc)} = \left(\frac{\partial F^{(exc)}}{\partial N}\right)_{VT}$

$$\mu = \mu^{id} + \mu^{exc} = kT \ln(\rho\lambda^3) + \mu^{(exc)}$$

The interesting quantity is $\mu^{(exc)}$

$$\mu^{(exc)}(N,V,T) = \left(\frac{\partial F^{(exc)}}{\partial N}\right)_{V,T} \approx \frac{F^{(exc}(N+1) - F^{(exc)}(N)}{(N+1) - N}$$

$$\approx F^{(exc)}(N+1) - F^{(exc)}(N)$$

$$= -kT \ln \frac{Z(N+1)}{V^{N+1}} + kT \ln \frac{Z(N)}{V^N}$$

$$= -kT \ln \left[\frac{Z(N+1,V,T)}{V Z(N,V,T)}\right]$$

We must evaluate the ratio in the square brackets

$$\frac{Z(N+1,V,T)}{V\,Z(N,V,T)} = \frac{\int dr_1 \dots dr_{N+1}\, e^{-\beta U(r_1 \dots r_{N+1})}}{V \int dr_1 \dots dr_N\, e^{-\beta U(r_1 \dots r_N)}}$$

Now, notation $\begin{cases} U(r_1 \dots r_{N+1}) = U_{N+1} \\ U(r_1 \dots r_N) = U_N \end{cases}$

and $V = \int dr_{N+1}$

so that

$$\frac{Z(N+1,V,T)}{V\,Z(N,V,T)} = \frac{\int dr_1 \dots dr_{N+1}\, e^{-\beta U_{N+1}}}{\int dr_{N+1} \int dr_1 \dots dr_{N+1}\, e^{-\beta U_N}} =$$

Correction: Here r_N+1 is r_N

$$= \frac{\int dr_1 \dots dr_{N+1}\, e^{-\beta U_N} \left(e^{-\beta U_{N+1}} e^{\beta U_N} \right)}{\int dr_1 \dots dr_{N+1}\, e^{-\beta U_N}}$$

$$= \left\langle e^{-\beta(U_{N+1} - U_N)} \right\rangle_{N + \boxed{1 \text{ particle free}}}$$

The average value is the usual average value for N+1 particles with Hamiltonian

$$U_N = U(r_1 \dots r_N)$$

PARTICLE (N+1) DOES NOT INTERACT WITH THE OTHERS

NOTE: for pair interactions

$$U_{N+1} - U_N = \sum_{j=1}^{N} V(\bar{r}_{N+1} - \bar{r}_j)$$

The IMPLEMENTATION

We only store the positions of the INTERACTING N particles.

A basic iteration is the following

(a) Perform N_{it} canonical MC steps for the first N particles [1 step ≡ update of one particle] [particle $N+1$ does not interact and therefore plays no role in the update of $\{\vec{r}_1, \ldots \vec{r}_N\}$] We use the canonical MC algorithm we have discussed before

(b) Perform N_r insertions of the $N+1$ particle and measure:

For $j : 1, \ldots N_r$

$\vec{r}_{N+1} = (L * RAN(), L * RAN(), L * RAN())$

compute $e^{-\beta U_{N+1} + \beta U_N}$ and store

END FOR

The ratio N_r/N_{it} can be optimized to obtain the smallest errors. Typically N_r/N_{it} is of order 1. [$N_r = 1.2\, N_{it}$, $N_r = 1.6\, N_{it}$, for example].